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By P. W. Bridgman.

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(Continued from page 3 of cover.)

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Introduction.

It is known that there is an intimate connection between the electrical and thermal conductivities of metals. This connection finds expression in the constant value of the Wiedemann-Franz ratio for different metals; the meaning of this is supposed to be that the largest part of the heat transfer in metals is accomplished by the same electrons which transfer the electricity in current conduction. I have already measured the effect of pressure on the electrical resistance of a large number of metals, and have drawn certain conclusions from the results as to the mechanism of electrical conduction.[1] It seemed that it would be no less interesting to measure the effect of pressure on thermal conductivity. This paper contains the results of measurements of the effect of pressures to 12000 kg/cm^2 on the thermal conductivity of lead, tin, cadmium, zinc, iron, copper, silver, nickel, platinum, bismuth, and antimony at 30° C.

At the time that I undertook these measurements this was an entirely untouched field; not even the sign to be expected for the effect was known. Since starting this work, measurements have been published by Lussana [2] on the effect of pressures to 3000 atmospheres

on the thermal conductivity of eight metals and four alloys. Except for two of the alloys, he finds that the thermal conductivity always increases under pressure, and the change is of such a magnitude that the Wiedemann-Franz ratio remains nearly constant. The classical conception of the mechanism of conduction would prepare one to expect this result. I have not been able to verify the results of Lussana, but find that the conductivity of more than half my metals decreases instead of increases under pressure. This is perhaps a result not to be expected, and must have considerable significance for our picture of the mechanism. With regard to the differences between Lussana's results and my own, I think that Lussana's work is open to serious criticism in several particulars, and I have gone into this in detail later.

Measurements of thermal conductivity are known to be among the most difficult in physics (witness the disagreement among different observers as to the sign of the temperature coefficient of thermal conductivity), and I was accordingly prepared for considerable difficulty in measuring changes, which might be expected to be of the order of a few per cent, in a quantity which is itself so hard to measure. The difficulties were of course enhanced by the technical necessity of making the apparatus so small that it could be enclosed in a pressure chamber. The anticipated difficulties were encountered; these measurements are by far the most difficult of any that I have attempted under pressure. The accuracy is accordingly much less than that possible in such measurements as of electrical resistance under pressure, for example. Certainly not more than two significant figures can be claimed for the pressure coefficient of thermal conductivity. If the work were to be repeated now it would be possible to improve considerably on the accuracy, or at least the presentability, of much of it. But I believe that the results which follow are essentially correct in their large features, and that the use which can at present be made of such data does not justify the expenditure of more time.

Description of Apparatus and Method.

The choice of methods was much restricted by the limitations of space imposed by the necessity of getting the specimen and all the attachments into a pressure cylinder, and by the necessity of using only four electrical leads to the heating element and thermo-couples. Two methods were used; these were both of the same general character

in that they carry the determination of thermal conductivity back to the definition. A known steady supply of heat was put into the specimen, and by means of a thermo-couple the difference of temperature was measured between two points when equilibrium was reached. In terms of the geometry of the configuration the temperature gradient and the rate of heat flow across unit area can be immediately found, and hence the thermal conductivity may be found from its definition.

The first method was in theory the simplest, as there were practically no corrections to be applied. This was a radial flow method. The specimen was in the form of a massive cylinder, almost filling the bore of the pressure cylinder. Along the axis of the cylinder was a linear source of heat, and the difference of temperature was measured between two points at different radial distances from the axis. The formula for thermal conductivity in this case is

$$k = \frac{Q}{2\pi(\theta_1 - \theta_2)} \log \frac{r_2}{r_1},$$

where k is the conductivity, Q is the heat input per unit length of the axis, r_1 and r_2 are the radial distances of the two junctions of the thermo-couple, and θ_1 and θ_2 are the temperatures of these two junctions.

The flow of heat under these conditions is radial, except at points near the ends of the cylinder. By locating the thermo-couple midway between the ends of the specimen any end effect may be avoided. The method is therefore unusual in that there is no correction for heat leak. Further there is no correction for the change of dimensions of the specimen under pressure, for it is only the ratio of the two radial distances that enters the formula, and this is not changed by a hydrostatic pressure which uniformly changes the dimensions in every direction. There is a correction in the heat input due to the change of length of the heating unit under pressure, but this correction is equal to the linear compressibility, and is so small as to be almost negligible. The heating element was made of nichrome. Assuming the compressibility of nichrome to be calculable by the law of mixtures from that of nickel and chromium, its two constituents, the magnitude of this effect is 0.2% under 12000 kg/cm^2. The correction is an addition to the observed pressure effect. There is also to be considered the change of resistance of the heating unit under pressure, but by a suitable arrangement of the circuits this may be made to eliminate itself, as will be seen later.

I designed this method of radial flow to meet the needs of the high

pressure measurements, and found only later that it had been previously proposed by Niven [3] in 1905, particularly for measuring the conductivity of comparatively poor conductors.

The method was used with many modifications, as will be described later. Its essential weakness is that it demands that the specimen be perfectly homogeneous; this is difficult to obtain in sufficient perfection in a casting, or even in commercial drawn metal. The method worked best for lead, which is fairly easy to cast, is a comparatively poor conductor, and is not crystalline, so that inhomogeneities due to crystallization during cooling were not important. The method failed for copper and nickel.

The second method was a longitudinal flow method. Heat is put into the end of a rod, the other end of which is connected with a massive copper block in intimate contact with the pressure cylinder, so that we have essentially a rod with a source at one end and a sink at the other. The difference of temperature between two points on the axis of the rod is measured with a thermo-couple. In contradistinction to the other method there is here an important correction due to the lateral loss of heat to the fluid by which pressure is transmitted. An elementary discussion shows that in order to reduce this correction to the smallest value it is necessary that the dimensions of the specimen be very small. The specimens actually used were only $\frac{1}{8}$ inch in diameter, a little over 1 cm. long, and the two thermal junctions were 2 mm. apart. The correction for lateral loss is evidently smallest for those metals with the greatest conductivity, so that this method supplements the other, working best for those metals for which the first method gave the poorest results. The magnitude of the correction for lateral loss may vary from 20% of the total effect for bismuth, to about 1% for copper and silver. The most disagreeable feature of this correction is that it changes with pressure because of the change of conductivity of the transmitting medium under pressure. This effect is large and has to be independently determined. The thermal conductivity of petroleum ether, which was the medium used in all the later part of this work, increases 2.2 fold under 12000 kg/cm^2. The determination of the pressure effect on petroleum ether will be described in detail later.

Discussion of further details of these two methods is reserved until later.

The electrical measurements involved in either method were essentially the same in character, and could be made with the same apparatus. The measurements necessary were of heat input, which

involved a knowledge of current and resistance, and of temperature difference, which demanded a measurement of the electro-motive force of a thermo-couple. Since it was necessary to find only the relative changes in thermal conductivity, a source of heat of unknown magnitude would have been sufficient, provided that it remained perfectly constant. The arrangement of the circuits, to be described in the next paragraph, ensured approximate constancy of the heat input, so that the measurements of the heating current degenerated to check readings from which a small correction was determined. The measurements of both heating current and e.m.f. were made on the same potentiometer as was used in previous measurements of the effect of pressure on thermo-electromotive force.[4] This apparatus has already been described in sufficient detail. By an arrangement of suitably protected switches either the thermo-couple or a small potential tap from the heating circuit could be connected in place of the couple as previously used. The tap in the heating circuit was constructed of heavy manganin wire of a resistance of approximately 1/13000 ohm.

Correction for the change of resistance of the heating element with pressure was avoided by using a similar heating element in shunt with the one exposed to pressure. The shunt unit was mounted in the same thermostated bath as the pressure cylinder, but was not exposed to pressure, so that its resistance remained constant during changes of pressure. By writing down the equations for the divided circuit, one can see in an instant that if the total input of current into the two heating elements in parallel is maintained constant, the rate of generation of heat in that one of the two elements which is exposed to small fluctuations of resistance remains constant. The total input of current was maintained approximately constant by using for the source of supply a storage battery in series with a ballast lamp (iron filament in an atmosphere of hydrogen) obtained through the courtesy of the General Electric Company. The total fluctuation of resistance in series with the lamp due to changes of pressure was only 0.08%, and with constant e.m.f. the lamp reduces the fluctuations of current due to this to negligible proportions. However, the battery itself was not always sufficiently constant, and in order to determine the small correction due to its fluctuations, the total current delivered by the battery was measured by determining the current in the two branches of the shunt. This was done with the potentiometer and a low resistance tap, precisely as for the heating circuit. The total corrections due to fluctuations in the heat input were always a small fraction of 1%.

A correction also had to be applied for the change in thermal e.m.f. of the couple under pressure. The couple was of copper-constantan, and the corrections due to pressure may be taken from data already published.[4] The total correction at 12000 kg. due to this effect is 0.8%; the correction is to be subtracted from the apparent thermal conductivity.

It will be noticed that this method differs from those previously used in determining the effect of pressure on electrical conductivity or thermal e.m.f. in that it is not a differential method, but is direct. A number proportional to the total thermal conductivity is determined at different pressures, and from these data the effect of pressure is computed. As originally planned I had intended to make the method differential, measuring the difference of thermal conductivity between one sample exposed to the pressure and a similar one not exposed. This can be simply done by opposing the two thermo-couples of the two specimens. It soon appeared, however, that the regularity of the results was not sufficient to justify this refinement, and the simpler direct method was used. The direct method demands somewhat greater accuracy in the resistances and the comparison standard cell, which, however, was easy to attain.

Since the primary interest of these measurements was in the proportional changes of thermal conductivity produced by pressure, a highly accurate knowledge of some of the absolute data was not essential. For instance, it is much easier to compare within 0.1% the two potential taps for the heating unit and its shunt than to measure the resistance of either accurately to 10^{-7} ohms, which would have been demanded by 0.1% on the absolute resistance.

We return now to a discussion of the details of the two different methods. First the radial flow method will be described.

The difficulties were chiefly mechanical, involved in getting the specimen into proper shape, and ensuring the right boundary conditions. The method demands not only that the heat input take place accurately on the axis, but most of all that the exterior surface of the specimen be maintained at constant temperature. The difficulty of this last requirement can be seen when it is considered that the thermal conductivity of copper, for example, is 3000 times greater than that of the petroleum ether by means of which pressure is transmitted to the specimen. There must of necessity be some crack between the walls of the pressure cylinder and the specimen; even if this crack is made vanishingly small at atmospheric pressure, it assumes quite appreciable proportions under 12000 kg. owing to the elastic deforma-

tion of the cylinder under internal pressure. If the specimen does not remain accurately centered in the cylinder at all times the flow of heat becomes unsymmetrical and the method is vitiated. Originally I endeavored to meet this condition by surrounding the specimen with a massive cylindrical sheath of copper, approximately $\frac{1}{8}$ inch thick. The specimen itself was $\frac{5}{8}$ inch in diameter and 2.5 inches long, and the interior diameter of the pressure cylinder was about $\frac{7}{8}$ inch. The crack between specimen and pressure cylinder was of the order of 0.005 inch initially, and it might increase by double under the extreme pressure. The use of the copper sheath is applicable only to those substances with low conductivity compared with copper. It might be expected to work best for lead and bismuth, and to work less well for tin and zinc.

Many variations were tried on this method. The chief difficulty proved to be that of getting good thermal contact between the specimen and the copper sheath. I at first tried to cast the easily fusible metals into the sheath. Unexpected difficulties were encountered in getting good enough contact. Casting into the bright sheath in air always introduced a film of oxide. Casting into the sheath in vacuum was tried, and also casting after making a preliminary coating of the interior of the sheath with solder or tin or the particular metal in question or silver plating, both in vacuum and a protecting atmosphere of illuminating gas. Satisfactory results were not obtained with any metal except lead. It was a surprise that it was so difficult to make good contact with tin.

A difficulty anticipated with this method because of the unequal compressibility of the copper of the sheath and the metal of the core did not turn out to be formidable; this difficulty could be turned by drilling the sheath with a number of fine holes so as to allow direct access of the pressure to the interior.

The device was tried of splitting the sheath into two pieces at a plane passing through the axis. In this way the inside of the sheath could be thoroughly tinned, as also the outside of the specimen, and by squeezing the specimen between the two halves of the sheath while still hot, good thermal contact could be secured initially. But with this arrangement the unequal compressibility of sheath and core was prohibitive; there was a progressive change with each application of pressure, the two halves of the sheath separating and working loose from each other. With tin, for example, a progressive change in the apparent effect of pressure on the thermal conductivity of three fold was produced by three applications of pressure.

The attempt to maintain the external surface at constant temperature by using a sheath was finally abandoned, and the specimen was maintained concentric in the pressure cylinder by an arrangement of springs. The specimen was made larger than when the sheath was used, being now only 0.02 inch smaller than the internal diameter of the pressure cylinder. Between the surface of the specimen and the walls of the pressure chamber were placed six longitudinal strips of german silver 0.002 inch thick, and about 0.42 inch wide. A sectional view through the specimen and the pressure cylinder is shown in Figure 1. The strips are shown bent to a nearly circular figure be-

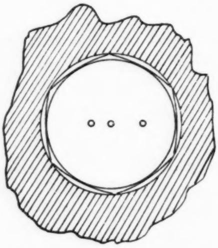

FIGURE 1. Section through the pressure cylinder and the radial flow specimen, showing the method of keeping the specimen concentric by springs.

tween the walls of the cylinder and the specimen. It is obvious that these springs will take up any stretch in the internal diameter of the cylinder, and maintain the specimen concentric at all pressures. The springs are so thin, and the thermal conductivity of german silver is so low that any error due to flow of heat away from the specimen through the springs is small, and need not be expected to change greatly with pressure. But as a precaution against any error from this effect the specimen was wrapped with a layer of paper between the springs and itself, thus minimizing any irregularity due to unequal heat loss at different parts of the surface of the specimen arising from inequalities in thermal contact between spring and specimen because of geometrical imperfections.

As far as I can judge, this method of maintaining the outer surface of the specimen as constant temperature was successful, but there were numerous other sources of irregularity. The chief outstanding mechanical problem now was that of getting the holes into the speci-

men for the heating element and the thermo-couple. The heating element must be of fine wire in order to have the requisite resistance, and the conditions of the problem demand that there be a cylindrical surface somewhere surrounding the heating element which is at constant temperature. That is, a surface at constant temperature is demanded both external and internal. I attempted to satisfy the requirement at the inner surface in the same way as at the outer surface by enclosing the heating element in a copper tube. The tube was small, usually about 0.040 inch outside diameter and 0.020 inch inside diameter. The outer surface of the tube was originally tinned and the specimen cast around it. I soon found the same difficulty in making good thermal contact as at the outer surface. If the specimen were melted after use and the copper tube examined it was very seldom that the surface was found completely wet with the metal of the specimen. But bad thermal contact at the center was not so serious as at the outer surface, because of the much smaller dimensions. Considerable improvement was made by using a tube of silver instead of copper. The difficulty here is due to the exceptional affinity between the silver and the metal of the specimen. If the mold is preheated, as is necessary to get a coherent casting, the alloying action between the metal and the silver is in many cases so great as to result in complete eating away of the silver tube. This effect was avoided by an arrangement of the mold by which the silver tube was drawn up into it from below after it was already filled with the molten metal, and the metal immediately chilled from the bottom up, so as to avoid the formation of blowholes. Specimens were made in this way and measured of lead, tin, and cadmium, but the method did not work with bismuth, the alloying here being so rapid that the silver was eaten away before the mold could be chilled.

The attempt to maintain internal equality of temperature by a tube of highly conducting material was finally abandoned, as it had been at the outer surface, and the heating element was placed directly in an axial hole made by casting the metal around a tungsten wire stretched along the axis during casting. The diameter of the nichrome heating element was 0.005 inch; this was enamelled, bringing the diameter to 0.006, and the diameter of the hole was 0.007, so that only a small amount of play was possible; furthermore the wire was always kept from direct contact with the specimen by at least the thickness of the enamel. This method of making the center hole could be used for all the metals that could be cast, including lead, tin, cadmium, zinc, bismuth, and antimony. With other metals of higher melting point

which were used in the form of cylinders the heating element has to be put in an axial copper tube. In these cases the axial hole was 0.040 inch in diameter, drilled through the specimen, which was then turned concentric with the hole, and the copper tube, which was not less than 0.039 inch in outside diameter, was then sweated into place. After some practise it was possible to get fairly good sweated contact. Since the pressure penetrates the interior of the tube, error from unequal compressibility of the two metals at the interior surface must be small. It is obvious that the use of an axial copper tube to contain the heating element can be unobjectionable only for those metals whose thermal conductivity is small compared with that of copper. The method cannot be expected to give good results for copper itself, for example.

The thermo-couples as well as the heating element were at first placed in two copper tubes cast into the cylinder, but this was later abandoned for a hole cast into the metal itself. In making the hole for the thermo-couple there are two opposing tendencies that must be guarded against. In the first place the wire of the couple must be so good a fit for the hole in which it is placed that the thermal conduction from the ends of the cylinder along the wires of the couple can be neglected. In the second place, if the fit is too close, pressure is not transmitted freely throughout the interior of the hole when pressure is high and the transmitting medium has acquired a certain amount of viscosity. Such viscosity results in the introduction of stresses into the wire, with an effective change in its thermo-electric constants, so that readings of temperature difference are no longer reliable. The attempt was made to meet these two opposing conditions by making the hole larger at the two ends with a narrow neck in the middle where the junction is situated. The cylindrical specimen itself was 2.5 inches long. The narrow part of the hole to receive the junction was 0.014 inch diameter and 0.5 inch in length. The larger part of the hole at each end was 0.040 inch diameter, and joined to the smaller part by a conical part 0.25 inch long, thus leaving the 0.040 part at each end 0.75 inch long. The diameter of the wire of the thermo-couple was 0.010 inch, and this was brought to 0.012 by the enamel. An approximate calculation shows that these dimensions are amply sufficient to prevent any appreciable flow of heat along the thermo-couple wire to the region of the junction, even with the metal of lowest conductivity. The hole was cast in the shape required by filing down a wire to a neck of the dimensions given at the middle, and holding this stretched through the mold in the required location. After the casting had been made, the wire was removed by pulling

out, the wire breaking at the narrow part, and allowing the two pieces to be pulled out separately from either end.

This method of casting the thermo-couple holes was of course not applicable to the metals with high melting points, and for these copper tubes sweated into place were used exactly as for the central heating element. The inside diameter of these tubes as used for this purpose was 0.016 inch. The junction of the couple was wrapped with fine wire in order to bring its diameter nearly up to the internal diameter of the tube, thereby preventing play in the tube and ensuring better thermal contact at the junction. In this case also the dimensions were such that any error due to flow of heat along the thermo-couple wire from one junction to the other was negligible. The results obtained with specimens made in this way are subject to a correction not easy to calculate for the disturbing effect of the copper tubes on the flow of heat. This correction should not be large because the

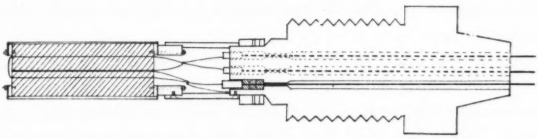

FIGURE 2. The radial flow specimen attached, with the electrical connections, to the insulating plug, ready to screw into the pressure cylinder.

copper tubes are comparatively small. The centers of the thermo-couple tubes were 0.098 and 0.201 inches respectively from the center of the specimen.

The electrical connections were got into the cylinder by means of a three-terminal plug of the same design as that used previously in determining the effect of pressure on electrical resistance by the potentiometer method. The only difference is that this plug could be made somewhat larger, because of the larger bore of the pressure cylinder, $\frac{7}{8}$ against $\frac{5}{8}$ inch. There is an advantage in this in that the thermo-couple leads can be got a greater distance from the heating element leads, and so there is less danger of heat leaking into the thermo-couple.

The manner of attaching the specimen to the plug ready for mounting in the cylinder is shown in Figure 2. The plug and specimen were attached together, and all electrical connections made before assembling so that the whole combination could be screwed into the cylinder as one self-contained unit. Attachments were made to the specimen

itself by three steel pillars 0.062 inch in diameter at either end. These pillars passed through washers of transparent bakelite at either end. At the lower end the bakelite washer was in turn attached to a thin steel sleeve, which was attached by screws to the three terminal plug. The screws connecting the bakelite washer to the steel sleeve were made a loose fit in order to allow sufficient freedom for the german silver springs to keep the specimen concentric in the cylinder. The german silver springs were soldered to thin discs of german silver drilled to slip over the three steel pillars at either end and held in position by the same nuts which held the bakelite washers. The steel sleeve was cut away on two sides, allowing the ends of the thermo-couple and the heating unit to be brought through the bakelite washer and soldered to the three terminal plug. As an additional precaution against leakage of heat from the heating element into the thermo-couple, two massive pieces of copper in the form of a double wall were placed entirely across the pressure cylinder between the terminals of the plug connecting the thermo-couple and those connecting to the heating element.

Two forms of heating element were used for these cylindrical specimens, according to whether there was an axial tube, or the heating element was mounted in a fine hole cast along the axis of the specimen. When the tube was used, the heating element was in the form of a hairpin of 0.005 inch nichrome wire. By means of a jig the wire was made accurately 5 inches long when straightened out, so that it would exactly occupy the length of the tube when bent double. It was silver soldered at either end to a half-round piece of copper filed from a $\frac{1}{8}$ inch copper wire. The whole arrangement was covered with five or six coats of insulating enamel baked on, having a thickness of about 0.0008 inch. After enamelling, the wire was bent double into the hairpin form, thus bringing together the two halves of the copper wire so as to form a single completely round piece $\frac{1}{8}$ inch in diameter. As an additional precaution the two halves of copper were frequently insulated from each other by a thin layer of mica. The two halves were then bound together into a single piece by wrapping with fine silk thread. The resistance of the copper terminal pieces is so much less than that of the nichrome element itself that there is only a very small error introduced by any generation of heat outside the element. The massive copper pieces were attached to the terminals of the three terminal plug by a short length of flexible conductor twisted out of many fine strands of copper. The total resistance of the heating elements made in this way was nearly 10 ohms.

If the specimen were one of those with a small hole cast along the axis the heating element was a single length of 0.0035 inch nichrome wire, coated with enamel as the hairpin unit, silver soldered at one end to a massive copper wire, and grounded at the other to the specimen itself by soldering to a piece of fine german silver sheet, which was in turn soldered to the specimen. By using an intermediate member of fine german silver sheet the difficulty of attaching the fine wire to the massive specimen at exactly the required point was obviated, and it was easy to make the heating element the same length as the specimen itself, at least within 0.002 inch, which was close enough. The specimen itself, which was grounded to the pressure cylinder, was used as the return connection for the heating element. In order to eliminate any danger of bad contact between the specimen and the cylinder, a connection was soldered to one of the steel pillars and the ground connection of the three terminal plug.

The thermo-couple, as already mentioned, was constructed of copper-constantan. Each couple was made of three pieces of wire, first a length of copper, then one of constantan, and then one of copper, of the same length as the first. This was bent into a hairpin form, and the two legs of the pin slid through the two thermo-couple holes. The dimensions were so chosen as to bring the two junctions copper-constantan midway between the ends of the specimen. The two copper ends of the couple were attached by solder to the two copper thermo-couple terminals of the three terminal plug. It is thus seen that the e.m.f. of the couple is determined by the temperature difference of the two copper-constantan junctions.

The wires of which the couple were made were 0.010 inch diameter. It is essential that the junctions be absolutely smooth butt joints. It is a little trick to successfully make these, but the following procedure finally gave satisfactory results. The ends of the wires to be united were first coated thinly with silver solder and borax, precisely as ordinary objects are "tinned" for soft soldering, by dipping into a drop of molten silver solder covered with a little borax. The drop of silver solder was maintained molten at the desired temperature in a miniature electric furnace made by winding nichrome wire around a core (of course insulated from it) of $\frac{1}{4}$ inch nichrome rod, in the end of which was drilled a shallow depression to hold the drop of molten solder. After coating the ends of the wires, they were brought into exact axial alignment in a clamp with three adjustments. The wires were held in pieces of quartz tubing drawn down to the proper size, and projected perhaps $\frac{1}{4}$ inch or less from the tube. The solder on

the ends of the wires was then melted and the wires fused together by a small blue gas flame. A flame of the required size may be obtained from a jet issuing from a piece of drawn out glass tubing. The gas to give the blue flame is supplied from a gasometer, which may be improvised from a couple of old tin cans, filled with a mixture in the right proportions of illuminating gas and air. The joint so formed is very strong mechanically. If the wires are not in satisfactory alignment they may be made so by hammering. The method is considerably superior to any simple electrical method of welding with which I am familiar. Of course there is no objection to smoothing the junction with a little fine emery paper; by this means a joint can be made that cannot be detected by the sense of touch, or of sight, after the wires are enamelled. The wires used were all cut to standard lengths by jigs, so that after enamelling the joints could be located by measurements. I have used this same method to make junctions as small as 0.004 inch, which are considerably more than two and one half times as hard to make by the ordinary method.

A great many measurements were made with specimens of the cylindrical form described above, and every effort was made to make the method give good results. The measurements with any one specimen were usually regular, and would repeat, and were apparently as good as could be asked. The trouble was that the numerical results obtained with different specimens of the same metal did not agree. The lack of agreement was much worse for some metals than others. I finally came to the conclusion that the method is essentially limited by the demands for homogeneity which it imposes on the specimen. Any slight flaw in the casting, resulting in cracks whose dimensions would change with pressure, must change the direction of the lines of flow with pressure. Further, any large scale crystal structure would give different results for different castings.

The second method was designed to obviate as much as possible the effect of inhomogeneity in the sample. As already mentioned, this is a longitudinal flow method, there being a source and a sink at the ends of the specimen, and the difference of temperature at two fixed points is measured. Since the heat input must cross each section of the specimen, any distortion of the flow by local inhomogeneities must have less effect than in the case of the cylinder, where as an extreme case it is possible that a flaw properly situated might force all the heat input to flow out of the cylinder at one side only. The much smaller dimensions of the longitudinal flow specimens would also seem to reduce the chance of errors from flaws.

A scale drawing of the longitudinal specimen mounted in the massive copper block ready for assembly in the pressure cylinder is shown in Figure 3.

The sink at one end of the specimen was formed by soldering it into a massive copper block of a diameter nearly the same as the interior of the pressure cylinder. Good thermal contact between the copper block and the cylinder was ensured by a centering arrangement of springs of strip metal, exactly as in the case of the cylindrical specimens, except that now the strips were made of heavy copper instead of thin german silver. In order to reduce mechanical distortion due to unequal compression of the specimen and the copper of the block, the bottom of the hole in the block into which the specimen was

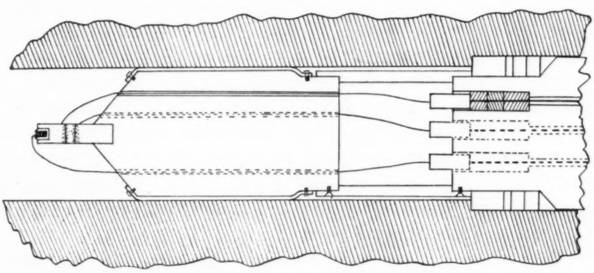

FIGURE 3. Longitudinal section of the pressure cylinder with the longitudinal flow specimen attached to the three terminal plug and in place.

soldered was brought into connection with the pressure transmitting medium by a small drilled hole.

The source of heat at the other end of the specimen was provided by a small coil of nichrome wire 0.005 inch diameter and exactly 1 inch long, silver soldered to copper leads of the same diameter. The resistance was of the order of two ohms. This wire was wound into a coil of small dimensions on a core of a fine piece of glass tubing, and was placed in a small copper capsule in the form of a square bottomed cup about 2.5 mm. deep. One end of the heating coil was grounded to the cup with solder, and the other end was connected to a lead from the three terminal plug. The copper capsule was let into a hole of the proper dimensions drilled in the end of the specimen. By the use of the capsule I hoped to more nearly realize a uniform heat input over the entire cross section of the specimen. To further realize these

conditions, and obviate irregularity due to poor thermal conduction of any transmitting medium which might get into the cracks between specimen and capsule, the capsule was cemented into the specimen with deKhotinski cement, which has a considerably higher thermal conductivity than the liquid.

It will be noticed that the method of connection described above amounts essentially to grounding one end of the heating element on the sample itself, there being effectively a junction between the metal of the specimen and copper. When a heating current is passed there will be a generation of Peltier heat at the junction in addition to the Joulean heat in the element itself. This effect reverses in sign when the direction of the heating current reverses and so may be eliminated. However in the experiment as actually performed the independence of the reading of the thermo-couple of the direction of the heating current was used as a criterion for absence of electrical leakage between the heating and the thermal current circuit, so that elimination of the Peltier heat by reversal of the heating current was not desirable. For most of the metals the effect is very small and may be neglected, but for antimony and bismuth the effect becomes inconveniently large, rising to a change in the apparent magnitude of the thermal conductivity of 25% with reversal of heating current. For these two metals the ground to the capsule was discarded, and two independent leads to the heating element were used.

The thermo-couple was constructed in the same way as those for the cylindrical specimen; a length of copper, then a piece of constantan 1 inch long, and then copper again. This was bent into the form of a hairpin, whose two legs were thrust through two diametral holes 2 mm. apart in the specimen. The junctions were located on the axis of the specimen. After wrapping the wires around the specimen, as will be described in a later paragraph, the two copper ends of the hairpin were then soldered to the two copper thermo-couple terminals of the three terminal plug. The thermo-e.m.f. of the couple obviously gives the difference of temperature of the two junctions points.

In order to avoid error from heat leak along the wires of the couple it was necessary to make these of much smaller wire than in the case of the cylindrical specimens. The wire used was 0.004 inch diameter, and the hole in which the couple was placed was 0.007 inch. The couples were brought to a diameter of 0.005 inch by the coating of enamel. There is an outstanding possible play of the couples in the holes of 0.002 inch, which might lead to maximum errors in the apparent thermal conductivity of 5%. This is probably the chief source

of error in this method, and it will be seen later that the results are consistent with this explanation. In some of the later measurements the attempt was made to cut down the motion possible in the thermo-couple by threading into the hole along with the couple a wire 0.002 inch diameter. In some cases this seemed to produce good effects, and in others apparently not. There is danger that too close a fit may introduce tensions into the thermo-couple, and so change its constants. It did not seem feasible to try for a much closer fit between the couple and the hole because of the difficulty of getting a perfectly smooth coating of enamel on the wire of the couple.

The specimens of the two soft metals lead and tin were cast, and the holes for the thermo-couple were cast with the specimens, using a 0.007 inch wire for the core, held in a proper position in the mold. For all the other metals the holes were drilled. A small jig was made and the holes were drilled in a jeweller's lathe. In spite of the use of the jig it was not possible to make all the specimens exactly alike, and the distance apart of the holes was independently measured in every specimen with a microscope. The extreme variation in their distance apart was from 0.190 to 0.210 cm. I found that a very convenient drill may be made of a piece of tungsten wire, pointed so as to form the conventional flat drill. The advantage of this over steel is that it is so tough that it is almost impossible to twist off, which may very easily happen to a steel drill in a clinging metal like gold, for example. While not as hard as steel, tungsten is hard enough to drill all the metals used here, which included iron, nickel, and platinum, all in the annealed condition.

Because the hole containing the couple is comparatively short, there is greater danger of error from heat leakage along the thermo-couple wire than in the first method. To eliminate this source of error, the wire of the couple was bent sharply at the entrance of the hole, at either end, and was wrapped once, or in some cases twice, about the specimen, and held in close contact with the external surface by a wrapping of fine silk thread. This ensures that the wire for some distance from each junction shall have the same temperature as the specimen at the junction, and so should eliminate error from leak. As an additional control with regard to heat leakage along the wire, the experiment was tried with two specimens of first using a couple constructed as above (constantan between two lengths of copper) and then a couple constructed of constantan between two lengths of "therlo." "Therlo" is an alloy made by the Driver Harris Co. with very nearly the same e.m.f. against constantan as copper, but with

a thermal conductivity at least fifteen times less. The error from heat leak along the wires of the couple should therefore be very much less with the therlo couple. As a matter of fact, the same results were obtained with both couples, establishing freedom from heat leak.

A central band of one or two coats of enamel (thickness not over 0.0001 inch) was usually baked on the outside of the specimen. This was to avoid danger of short circuit where the thermo-couple wires were wrapped about the cylinder. Baking on this band of enamel, which required about 210° C, served the additional purpose of annealing the specimen. All the specimens were further heated to 150° or so when soldered into the massive copper block.

As already explained, the dimensions were forced by compromise between various opposing tendencies. If it were not for lateral loss, the specimens would have been made much longer, and the source and sink would have been situated further from the couple. This would have allowed the lines of flow to more completely straighten out in the vicinity of the couple. It is possible by a rough calculation to get an approximate idea of the extent of the failure of the lines of flow to be entirely straight. The actual distribution of temperature over the section at the source end cannot of course be accurately determined, but it seems fair to assume that the temperature is higher at the center of the rod than at the outside surface. A solution corresponding to this state of affairs may be obtained by assuming a distribution of temperature according to a Bessel's function over the source end. I carried through an approximate examination in this way, and convinced myself that any errors from this effect were not important.

The largest correction to be applied in the longitudinal flow method is for the lateral loss of heat through the transmitting medium. The lateral loss is a small part of the total input, so that we may assume the distribution of temperature approximately linear along the specimen. The temperature gradient at the mean point between the two junctions is the difference of temperature divided by the distance between the junctions. The total flow of heat long the rod at this point under this gradient is not the total input, because there has been some lateral loss between the source and the junction. This loss takes place partly from the lateral curved surface, and partly from the end. The loss from the lateral curved surface of the bar was computed on the basis of the formulas for the radial flow of heat through a cylinder between inner and outer surfaces maintained at constant difference of temperature. The temperature of the inner surface, that is, the temperature of the bar, varies along the axis. The total lateral loss

was taken as the integral of the losses of short elementary cylinders. The loss from the upper end was calculated from the formula for the flow between two concentric hemispheres, one having the radius of the specimen, and the other the internal radius of the pressure cylinder. The value obtained in this way is obviously too large, as most of the pressure cylinder is situated further from the end of the specimen than its internal radius. The lateral flow and the flow from the ends as computed in this way involve the difference of temperature between the source end of the specimen and the outer cylinder. This temperature difference may be expressed approximately in terms of the heat input into the rod and the thermal conductivity of the rod. The temperature difference may now be eliminated, giving a result in terms of heat input and the conductivities of the liquid, k_2, and the metal of the bar, k_1. For the lateral loss of heat I obtained the formula $11.7\frac{k_2}{k_1}Q$, and for the loss from the end $12.\frac{k_2}{k_1}Q$ (this last is too high). As an approximate value for the total loss through the transmitting medium the value $20\frac{k_2}{k_1}Q$ was used in the computations.

The value of k_2, the thermal conductivity of petroleum ether, was determined by direct experiment, as will be described later. At atmospheric pressure the value found was 0.0004. At a pressure of 12000 kg/cm^2 the conductivity has increased 2.2 fold. The change in the value of the lateral flow correction with pressure determines the correction that must be applied to the apparent change of conductivity of the metal under pressure in order to obtain the true change. The magnitude of this correction evidently changes greatly with the metal used. The details with regard to this correction will be discussed under the different metals separately.

In the longitudinal flow method there is no correction to be applied for the change in dimensions of the heating element, as there was in the radial flow method. The same arrangement of a shunt circuit which eliminated the necessity for a correction for the changing resistance of the heating element with the radial flow method was used here also. There is a correction to be applied here, not necessary in the radial flow method, for the change of dimensions of the specimen under pressure. Under pressure the cross section becomes less and the distance between the thermal junctions also becomes less, the first by twice the linear compressibility and the second by the linear compressibility. The sum of the two effects is a correction equal to the

linear compressibility in the direction of an increase to the apparent conductivity. In the absence of direct determinations of compressibility at high pressures, the corrections applied in the following were then taken from Richard's determinations at low pressures, neglecting the changes of compressibility with pressure. The correction is in any case small; the value for bismuth is a maximum at 1.2%. In addition to these corrections there was an effect not present appreciably with the radial flow method due to loss of heat along the leads to the heating element. The leads were of copper and the heating element was of nichrome. The thermal conductivity of copper is about 30 times and the electrical conductivity about 50 times that of nichrome. Hence most of the heat input is confined to the nichrome and there cannot be much heat conduction out along the leads; any cooling of the copper leads can affect only the extreme ends of the nichrome coil. The correction for this effect must be small, but may affect the absolute conductivity. Only the change of this correction with pressure can affect the final results, and I have neglected it.

There is one source of error that might be anticipated to be serious with the longitudinal flow method, namely convection effects in the liquid. In any event the convection effects may be expected to vanish at high pressures because of the known large increase of viscosity of the transmitting medium. I did expect the effect to be appreciable at atmospheric pressure, however, and at first made no reading at atmospheric pressure, but used 2000 kg. as the zero. It later appeared, however, that points obtained at atmospheric pressure lay on a smooth curve with those at higher pressures, so that no error from this effect is to be expected. It is in any event to be remarked that the error from convection may be made vanishingly small by cutting down the heat input. Assuming that the convection loss is only a small part of the conduction loss, we see that if the heat input is halved the temperature differences in the liquid are halved, the rate of convective flow of the liquid is halved, and the rate of heat flow into the liquid is halved, so that the total heat carried away convectively is quartered. (Of course the loss of heat by conduction to the liquid is only halved). In the actual experiment the magnitude of the heating current was so chosen that the temperature of the source end of the specimen was about 5° higher than that of the pressure cylinder. In one or two cases parallel runs under pressure were made with changes in the heat input by a factor of 2, with no change in the results. Also at atmospheric pressure I verified that the temperature difference measured on the thermo-couple was proportional to the square of the

heating current. Both of these checks prove freedom from convective effects.

The longitudinal flow method showed itself a great improvement over the radial flow method with regard to the agreement of the results obtained with different specimens of the same metal. The individual readings for a single specimen, however, were very much more irregular, and until the interpretation of the irregularities was found, I was in doubt whether this method was actually any improvement over the previous one or not. After readings had been made on a number of specimens, it appeared that in almost all cases the readings for a single specimen would lie on three or perhaps four straight lines. The extreme separation of these lines amounted to a difference of not more than 5% in the total thermal conductivity. It has already been mentioned that this is the variation which might be caused by a shift of position of the thermo-couples in their holes. The natural interpretation is that the couple may take one of two extreme positions, like the bottom of an oil squirt, bent so as to touch either the top or the bottom of the hole. The couple may change from one to the other of these positions with change of pressure. The two couples together can thus occupy any one of three different positions, so that the readings will lie on one of three lines. If the initial curvature of the wires of the couples is such that one of the positions of equilibrium is not exactly at the top or bottom of the hole, then there will be four relative positions of the couples, and the results will lie on four lines, two of them comparatively close together. Figure 9, given later in the detailed discussion of the data for nickel, is a good example of the tendency to lie on discrete lines.

After the reason for the irregularities had been found it was possible to a considerable extent to control the location of the readings on one or the other of the possible lines. It was found, as might be expected, that rapid changes of pressure were favorable to a jump of the readings from one line to another, but that by changing the pressure very slowly it was in many cases possible to obtain long successions of points on a single straight line. It is easy to see that the nature of the irregularity is such that it was quite possible, before its true nature was recognized, to obtain results which might be erroneous even as to the sign of the effect. Suppose for example that the true effect gives points lying on a falling curve, but that as pressure increases the thermo-couples snap over in the holes in such a way as to pass from the low lying to the high lying curves. If only a few readings are taken, and if the snapping about of the couples is a fairly regular

matter, as it often is, it can be seen that a regular succession of points may be obtained apparently lying on a rising curve. To avoid error from this effect each individual set-up demanded individual study, as the way in which the wires snap about is an individual matter. The true curve can be found by taking a larger number of readings than at first I thought necessary, and by studying the possibilities of obtaining successions of points on single straight lines under very slow changes of pressure. In one or two cases, after the effect had been recognized, it was found that the results originally obtained were in fact of the wrong sign, and that on setting up the specimen again and carefully analyzing the situation the correct result indubitably appeared of the opposite sign. Examples of this will be mentioned later.

Experimental Procedure.

The procedure for either the radial or the longitudinal flow method was essentially the same. The specimen was first attached to the three terminal plug, connections to the interior end of the plug being made with solder. The plug with the specimen in place was then screwed into the pressure cylinder, and connections made to the outer end of the plug by soldering. The temperature bath was then put in place, and temperature adjusted to 30°, which was the universal temperature of these experiments. (The accuracy was not great enough to justify an attempt to determine the temperature coefficient of the pressure coefficient, such as had been possible in the case of the measurements of electrical resistance, for example.)

The heating current was now turned on and equilibrium waited for, as shown by the constancy of readings of the thermo-couple. An interval of 20 or 30 minutes was necessary to reach initial equilibrium after adjusting the temperature bath. This time was nearly all consumed in acquiring equilibrium throughout the interior of the pressure cylinder, and particularly between the outer and inner ends of the three-terminal plug. The leads through the plug were of necessity of steel in order to obtain sufficient strength, whereas the metal at either end of the plug was copper. Hence any temperature inequality between different parts of the plug introduces spurious e.m.f.'s into the circuit, so that it is essential to wait for complete equilibrium. As far as the specimen itself and the heat flow through it from the heating element is concerned, equilibrium was attained very quickly. If the heating current was turned on or off after the bath and cylinder had

reached equilibrium, the thermo-couple reached equilibrium in a fraction of a minute in the radial flow method, and in at most two or three minutes in the longitudinal flow method.

While the bath was coming to temperature equilibrium, I usually made a preliminary application of 12000 kg. to be sure that the joints were tight, and that the electrical insulation resistance between the heating element and the thermo-couple circuit was sufficiently high. The insulation resistance was measured independently of the potentiometer, and had in all cases to be as high as 100 megohms if satisfactory results were to be obtained. The pressure transmitting medium in all these experiments was petroleum ether. The use of this was necessary to avoid stresses in the couples introduced by viscosity effects. The mechanical difficulties of retaining this liquid under pressure without leak are very materially greater than for the mixture of ether and kerosene which I had used before. Slight mechanical imperfections in the bearing surfaces become much more important, so that the preliminary test for leak on the whole saved time. There did not seem to be any seasoning effect proper produced in the specimen itself by the initial application of pressure, as indeed there ought not to be if the specimen is homogeneous and well annealed. In a number of cases when the radial flow method was used and the specimen was mounted in a copper sheath, the specimen was seasoned by several applications of the maximum pressure before any of the electrical connections were made. Seasoning in this case was necessary because of unequal compressibility of the specimen and the copper of the sheath.

After reaching equilibrium at atmospheric pressure, the pressure zero was read. The magnitude of the current in the heating element and its shunt was then read on the potentiometer, both for the direct and the reversed direction of the heating current. The reversal of the heating current was accomplished with a double pole double throw switch and took place so quickly that there was no appreciable interruption in the heat input. The mean of readings with direct and reverse heating current eliminates the effect of any parasitic thermal e.m.f.'s in the heating circuit. The final reading made was that of temperature difference on the thermo-couple. This reading was also made with both direct and reverse direction of the heating current. Any error from electrical leakage from the heating circuit (in which the current is of the order of 0.5 amperes) into the thermo-couple circuit (in which the e.m.f. is of the order of a few microvolts) because of defective insulation, is thereby eliminated. The reversal of the

heating current does not eliminate the effect of spurious e.m.f.'s in the thermo-couple circuit. There were no such spurious e.m.f.'s of detectible magnitude in the circuit in the absence of the heating current, as could be checked by the complete vanishing of the thermal e.m.f. on breaking the heating current. The only assurance against spurious e.m.f.'s introduced by the heating current itself was in the careful design of the apparatus. I could think of no way of making a direct check of this point without being able to introduce a cooling equal to the heating. In addition to the measurements above, as a rough check, the total current output from the storage battery into the ballast lamp was read on a commercial ammeter.

The pressure was then changed, usually by a step of 2000 kg., and after attaining equilibrium, the same succession of readings was again made. An interval of about 15 minutes was usually sufficient for equilibrium. This time is required to dissipate the heat of compression in the liquid and to again attain complete equality of temperature at the outer and inner ends of the three terminal plug. The usual routine consisted of two complete sets of readings to 12000 kg. and back. The results were plotted roughly as soon as obtained, making correction for any slight changes in the heating current and for fluctuation in the temperature of the copper coils of the potentiometer. This last correction was usually not necessary. When using the longitudinal flow method, after the cause of the irregularity of the readings was discovered, the plotted results were used to best direct the subsequent changes of pressure. The final computation of the results and the application of the other corrections which have been described above was made later.

The detailed data for the different metals follows.

Detailed Data.

Lead. More readings were made on this metal than on any other, and in general the results are better and the final result is probably more accurate than for any other. Nearly all the readings were made by the radial flow method, to which this metal is best adapted, because of its comparatively low conductivity.

Three grades of metal were used. A first rough trial was made with ordinary commercial lead. Several of the early measurements, in which a copper sheath was used, were made with so-called test lead from Eimer and Amend. The majority of the measurements, how-

ever, were made on lead of unusually high purity provided by the Bureau of Standards for the calibration of thermo-couples by the melting point. The analysis of this lead was as follows:

Ag .0002 – .0003%, Sb .0019 – .0028%, Sn .0008 – .0011%, Cu .0003 – .0004%, Fe. .0004 – .0006%, As, Bi, Zn, Co, Ni, trace, Cd, Mn, none; Lead (by difference) 99.9948 + %.

The melting point according to the certificate of the Bureau was 327°.3.

The accidental errors in the measurements were greater than differences due to slight amount of impurity, since all varieties of metal gave essentially the same results. The results are summarized in the following table.

TABLE I.

SUMMARY OF RESULTS FOR LEAD.

Description of Specimen	Percentage Change of Conductivity for 12000 kg/cm²
Solid Cu sheath, 3 copper tubes, commercial	21.5
" " " " " " "test"	20.2 19.2
" " " central Cu tube, "test"	23.6
Split Cu sheath, central Ag tube, Bur. Stds.	23.6 20.2
Large cylinder, no sheath, central Ag tube, Bur. Stds.	21.8 23.8
" " " " " " " " "	19.7 20.2 (12.1)
" " " " 0.007″ central hole, Bur. Stds.	18.7 20.0
" " " " " " " " "	16.5
Longitudinal flow, Bur. Stds. holes cast in specimen	20.9
" " " " " " " "	(8.1)
Average	20.7

In the above table, those specimens for which the nature of the central tube only is specified had the thermo-couple holes cast in the body of the metal in the isthmus shape already described. The

figures in parentheses in the table were omitted in taking the average, as evidently they are affected by some large error.

Of these measurements the best was the second run with the first specimen with the 0.007″ central hole. It is indeed to be expected that this manner of mounting the specimen would give the best results. The individual readings of this run are reproduced in Figure 4.

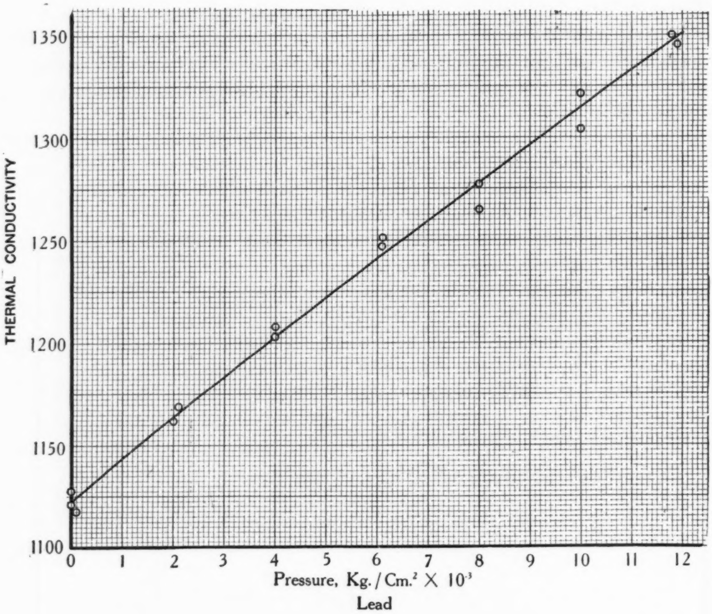

FIGURE 4. Lead. Thermal conductivity on an arbitrary scale against pressure in thousands of kg/cm². These results were obtained with a radial flow specimen.

The first of the two sets by the longitudinal flow method comes next in order of consistency, the individual points of this run lying even more nearly on a smooth curve than those shown in Figure 4, except for the initial point at atmospheric pressure, which lay off the curve by a large amount. The readings on the second longitudinal sample were not good for some unknown reason; possibly there may have

been flaws in the casting, as was indeed found to be the case one or two other times when the longitudinal specimen was cast. For lead, the correction to be applied to readings on the longitudinal specimens for the lateral flow through the transmitting medium was unusually large, reducing the observed effect from 30% to 20%.

The readings on the two best samples were sufficiently good to show a departure from linearity with pressure, the slope becoming less at the higher pressures. This is as would be expected. Part of the departure from linearity is without doubt to be ascribed to the effect of the transmitting medium, and since for most of the other metals the accuracy was not great enough to show this departure from linearity, it did not seem worth while to attempt to establish it more exactly for lead.

It will be seen that the two best runs agree pretty closely with each other and with the mean of all the measurements, so that considerable confidence may be given to the average value, 20.7%, as the most probable effect of 12000 kg. It is to be remarked that this change of thermal conductivity is markedly greater than that of electrical conductivity under the same pressure, which is only 14.6%.

The average pressure coefficient of thermal conductivity per kg. change of pressure is 0.0000173. Lussana [2] found as the average coefficient between atmospheric pressure and 2600 kg., 0.0000134. His initial coefficient was 0.0000164, and the final 0.0_4116, showing departure from linearity in the same direction as I found, but much greater in amount. His results do not show, however, any departure from linearity in this range in the relation between pressure and electrical conductivity.

Tin. A few preliminary measurements were made on tin with "chemically pure" metal from Eimer and Amend, but all the results of any value were obtained with Bureau of Standards tin, prepared for the calibration of thermo-couples by means of the melting point. The analysis of the tin was as follows: Pb .007%, Cu .003%, Fe .002%; As, S trace; Sb, none; Tin (by difference) 99.988%, and the melting point given by the Bureau's certificate was 231°.9.

Twelve different samples of tin were used, ten by the radial and two by the longitudinal flow method. None of those specimens in which a copper sheath was used gave results of any value whatever. The reason for this has already been discussed; the effect is due to lack of good thermal contact between the tin and the sheath. Neither was it found possible to get any results of value with those specimens in which the heating element was enclosed in a central silver tube. For

some reason it was not possible to make such good contact between silver and tin as between silver and lead. It may be that the greater ease of alloying between silver and tin resulted in inhomogeneity of the casting in the neighborhood of the central tube. Fairly consistent results were obtained, however, from those castings in which the heating element was placed in an axial hole 0.007 inch in diameter cast with the specimen. The results with the poor specimens which were discarded varied from 9 to 45% (the latter was for the split sheath which showed a progressive change with successive applications of pressure). The results with the better specimens are shown in the table.

TABLE II.

Summary of Results for Tin.

Description of Specimen	Effect of 12000 kg/cm^2
Large cylinder, no sheath, 0.007″ central hole............	15.4%
" " " " " " "	14.2 13.6
" " " " " " "	18.4 18.1
Longitudinal flow, all holes cast in specimen.............	11.1
" " " " " " "	11.9
Average	14.7

It is to be noticed that the results with the longitudinal flow specimens are lower than those for the radial flow specimens. The individual readings were not so good by the longitudinal method. It would perhaps have been better to have used a piece of extruded tin wire rather than the casting, in order that the specimen might be more homogeneous. The correction for lateral flow in the longitudinal method was 4.3 %, about a quarter of the total effect as measured. It is further to be noticed that the readings on the radial flow specimens which were repeated agree with each other more closely than they do with the mean, so that apparently the differences between the specimens are real. This may perhaps be partly ascribed to the effect of crystalline structure. Tin does not crystallize in the regular system, and is distinctly more crystalline in character than lead, for example, so that it is not surprising that there should be differences.

The best results were obtained with the first of the radial flow specimens listed above. The results with this specimen are reproduced in Figure 5. The same departure from linearity which was shown by lead is shown here also.

The average of the results listed above gives a mean pressure coefficient to 12000 kg. of thermal conductivity of $+ 0.0_4122$ per kg/cm^2. The corresponding coefficient of electrical conductivity is $+ 0.0_5929$.

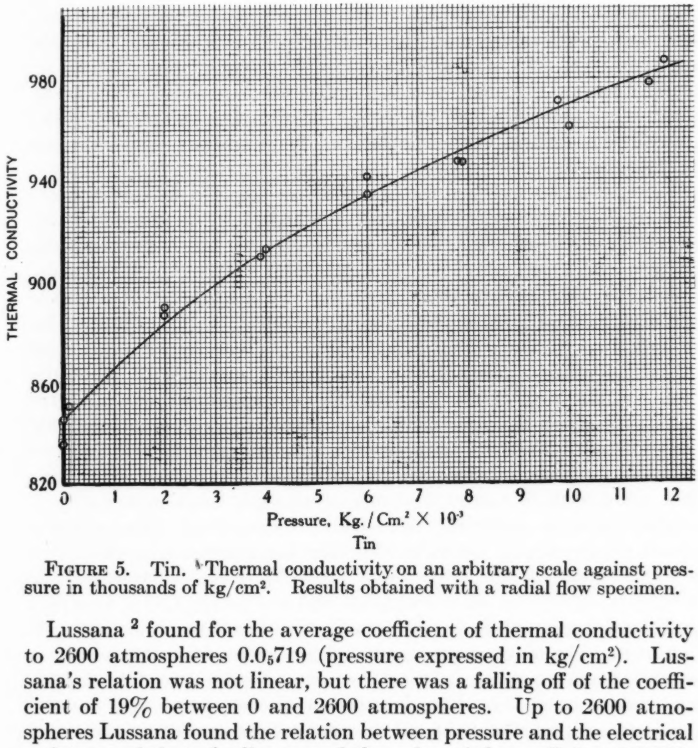

FIGURE 5. Tin. Thermal conductivity on an arbitrary scale against pressure in thousands of kg/cm^2. Results obtained with a radial flow specimen.

Lussana [2] found for the average coefficient of thermal conductivity to 2600 atmospheres 0.0_5719 (pressure expressed in kg/cm^2). Lussana's relation was not linear, but there was a falling off of the coefficient of 19% between 0 and 2600 atmospheres. Up to 2600 atmospheres Lussana found the relation between pressure and the electrical resistance of tin to be linear, and the value of the coefficient 0.0_5820. In my previous work I have found the relation to be sensibly not linear, and the initial value of the coefficient to be 0.0_41055.

Cadmium. The material used for the experiments was "chemically pure" cadmium from Eimer and Amend. I have no analysis. In all, eight sets of readings were made, four by the radial flow method, and four by the longitudinal flow. In general the results were not good. A number of smooth curves were obtained by the radial flow method, but the numerical values for the different specimens varied greatly, the extremes being 5.0 and 31.5%. One of the radial flow specimens had a central silver tube to contain the heating element; the results with this were very irregular. The three other specimens had a 0.007 inch central hole, and the results with them were not so irregular. The best mean values with the four radial flow specimens were respectively 5.8, 26.7, 4.2, and 14.8%. The mean of these is 12.9%, or discarding the highest as differing too much from the others, the mean of the three remaining is 8.3%. Doubtless much of the irregularity in the results by the radial flow method was due to imperfections in the castings.

The individual readings for any one specimen by the longitudinal flow method were widely scattered, and would not give much confidence in the correctness of the result if it were not for the fact that the different specimens gave results in agreement. The longitudinal flow specimens were two of them cast and two extruded. One of the castings was annealed at 130° for 30 minutes, the other not. The extruded specimens were seasoned by a preliminary application of 12000 kg. These differences in treatment seemed not to affect the results. The last of the longitudinal flow specimens did not give results of value; the other three specimens gave changes under 12000 kg. of 9.0, 8.7, and 8.7% respectively. The magnitude of the correction for the pressure effect on the petroleum ether was 3.8%. The best mean coefficient from these measurements is taken to be 8.9%.

The pressure coefficient of thermal conductivity given by the above mean value is $+0.0_574$. For the mean pressure coefficient of electrical resistance between 0 and 12000 kg. I found 0.0_5932. The results for the effect of pressure on thermal conductivity were not sufficiently accurate to establish any departure from linearity with pressure. The effect of pressure on electrical resistance becomes less at the higher pressures; I found the initial coefficient to be 0.0_41085, and the mean 0.0_5912. These results may be compared with those of Lussana. Up to 3000 he found the effect of pressure on both thermal and electrical conductivity to be linear; the coefficient of thermal conductivity he found to be 0.0_4122, and of electrical conductivity 0.0_592. The first is higher than my value, and the second lower. Lussana's value for the pressure coefficient of thermal conductivity

would be lowered by about 5% if my correction for the effect of pressure on the thermo-couple is applied. Lussana applied no such correction.

Zinc. Runs were made on three samples by the radial flow method, and two by the longitudinal method. The radial flow results were valueless; there is considerable difficulty in making homogeneous castings. The longitudinal flow specimens were extruded hot, and should be sufficiently homogeneous. The material was obtained from the Bureau of Standards, one of their melting point samples, and had the following analysis: Fe .005%, Pb .0004%, Cd .0018%, As, S trace; Sb, Sn none; Zinc (by difference) 99.993%. Melting point 419°.4. The results obtained with the two longitudinal samples were scattering, the points lying on several distinct lines, as already explained, but the correct slope could be picked out with some assurance. The change produced by 12000 kg. was 2.4% for one sample, and 2.7% for the other. Take as the mean 2.5%. The correction for the pressure effect on the transmitting medium was 3.0%, reducing a directly observed effect of 5.5% to 2.5%.

The pressure coefficient of thermal conductivity given by the above is $+0.0_521$. I had previously found the pressure coefficient of electrical resistance for a pressure range of 12000 kg. to be -0.0_5463. Lussana, over a pressure range of 2600 atmospheres, found the effect of pressure on thermal conductivity to fall off slightly from linearity, and the mean coefficient to be 0.0_541. The pressure coefficient of electrical resistance he found to be -0.0_5602; this relation he found to be sensibly linear.

Iron. Two samples were made for the radial flow method, and four for the longitudinal. The radial flow results were unsatisfactory. The thermo-couples and heating element were placed in copper tubes sweated into larger holes drilled in the specimen. The results were irregular, and the irregularities repeated themselves, showing that the effect is real, and denotes some defect in the specimen, not in the accuracy of the measurements.

Two of the longitudinal flow specimens were made from American Ingot Iron, from the same piece as the wires whose pressure coefficient of resistance and thermal e.m.f. have been previously measured.[4] The total impurity in this iron was not over 0.03%. The other two samples were made from a small sample of electrolytic iron of high purity for which I am indebted to the Bureau of Standards. The analysis of this iron is as follows:

Carbon	0.005	per cent.
Silicon	0.007	"
Sulfur	0.011	"

For some unknown reason the readings on one of these four samples were not satisfactory. The readings on the other three were quite typical of the results by this method, lying on one of several discrete lines. The results obtained with one of these are reproduced in Figure 6. The observed effect for iron is an increase of apparent conductivity of between 5 and 6% under 12000 kg., but the correction for the effect of pressure on the transmitting medium is so large, 5.3%, as to wipe out nearly all the observed effect. The results obtained

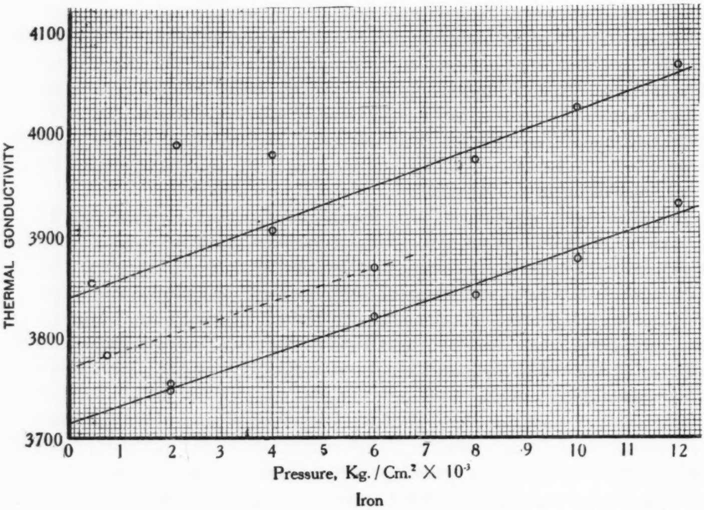

FIGURE 6. Iron. Thermal conductivity on an arbitrary scale against pressure in thousands of kg/cm². Results obtained with a longitudinal flow specimen. The points lie on several lines of the same slope; the reason for this is explained in the text.

with the three good samples, after applying all corrections, were −0.6, −0.2, and −0.2% respectively. The discarded data were not inconsistent with these values. We take as the mean −0.3%.

The pressure coefficient of thermal conductivity given by the above results is -0.0_63. I found for the pressure coefficient of electrical conductivity between 0 and 12000 kg. $+0.0_5229$. Iron is not one of the metals measured by Lussana, so there are no previous values for comparison.

Copper. Two specimens were made for the radial flow method, and four for the longitudinal. As in the case of iron, the thermo-couples and heating element of the radial flow specimens were placed in copper tubes sweated into place, and the results were not at all satisfactory. The points were not regular, and the irregularities repeated, showing some real effect. Furthermore, the two radial flow specimens were made from contiguous lengths from the same piece of commercial drawn rod, and the irregularities were much the same in character for each specimen, showing a real effect of inhomogeneities in the metal.

The four longitudinal specimens were made from electrolytic copper which I obtained a number of years ago from the Bureau of Standards.

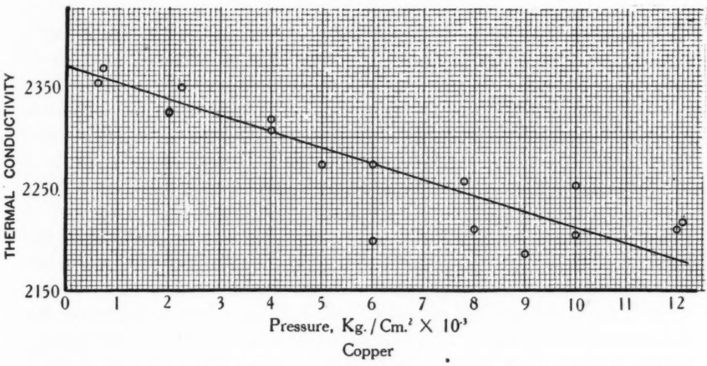

FIGURE 7. Copper. Thermal conductivity on an arbitrary scale against pressure in thousands of kg/cm². Results obtained with a longitudinal flow specimen.

Their analysis is as follows: Cu 99.995 per cent, trace S, no Ag, Cu_2O, As, or Sb. It is to be noticed that the purity is unusually high.

Measurements were made on some of these samples in the annealed condition, and others not; there seemed to be no difference in the results.

These four samples gave fairly good results, the points lying on discrete lines, as usual. The least scattering of these is reproduced in Figure 7. The effect is seen to be fairly large, and *negative*, the mean effects shown by the four samples were −9.7, −8.2, −8.3, and −7.5% change respectively under 12000 kg/cm². The mean is −8.4%, but we will take as the best result −9.0% instead, because

the best of the specimens gave the higher results. Because of the high conductivity of copper, the correction for the transmitting medium is small, being only 1.2%.

The pressure coefficient of thermal conductivity deduced from the data above is -0.0_575. No departure from linearity could be detected. I have found for the effect of pressure on electrical conductivity over this range the mean value $+0.0_5181$. Lussana's results for copper run only to 1000 kg. He found the effect to be linear, and the conductivity to increase under pressure, the opposite sign from my results. His coefficient is $+0.0_510$. The relation between pressure and electrical resistance he also found to be linear, and the coefficient to be 0.0_5212.

Silver. Only the longitudinal flow method was used on this metal. The material was obtained from Baker, and was said to be of high purity, but I have no analysis. Three different samples were used. The two runs made on the first two samples apparently indicated an increase of conductivity under pressure. The reason for this has been discussed in detail previously; not enough readings were taken, and there was a tendency for the points to shift from a lower lying to a higher lying curve with increase of pressure, thus simulating a false effect. More readings were made on the third sample, and an effort made to control the position of the points on one or another of the possible lines. The results with this sample are reproduced in Figure 8. The tendency of the points to lie on one or another of three distinct lines is obvious, as also the fact that the effect is negative, the conductivity decreasing with increasing pressure, instead of increasing, as was indicated by the results first obtained. The two first samples were now set up again, and the measurements repeated, with the precautions which had been gained from the intervening experience. The results shown by these two samples were now also unmistakably negative, and of nearly the same numerical value as shown by the third sample. The numerical magnitude of the total decrease of conductivity under 12000 kg/cm^2 shown by the three samples was 4.1, 4.4, and 4.6% respectively. The correction for the pressure effect on the transmitting medium was 1%.

The pressure coefficient of thermal conductivity given by the above data is -0.0_537. The average pressure coefficient of electrical conductivity between 0 and 12000 kg. I have found to be $+0.0_5334$. This metal was not investigated by Lussana, so there are no previous results for comparison as to the thermal conductivity.

Nickel. Both methods were used for this metal, and material from

two different sources. I am indebted to the International Nickel Co. for a piece of $\frac{7}{8}$ inch round rod of high commercial purity (99%). From this two samples were made for the radial flow method, large cylinders without the sheath. The thermo-couples and heating element were placed in fine copper tubes sweated into place. The results obtained with these samples were very irregular, and it was evident that the thermal contact between the copper and the nickel was not sufficiently good. These measurements did little more than establish a strong probability that the effect was negative. After the radial flow measurements had been made, two small pieces were

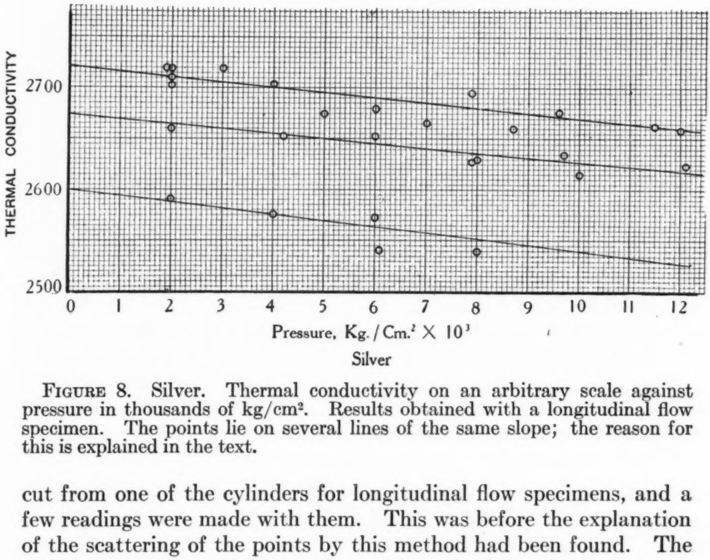

FIGURE 8. Silver. Thermal conductivity on an arbitrary scale against pressure in thousands of kg/cm². Results obtained with a longitudinal flow specimen. The points lie on several lines of the same slope; the reason for this is explained in the text.

cut from one of the cylinders for longitudinal flow specimens, and a few readings were made with them. This was before the explanation of the scattering of the points by this method had been found. The results were very scattering, and repetition would have been necessary to make sure of even the sign of the effect.

After completing the measurements on commercial nickel I was fortunate enough to obtain through the kindness of Mr. I. B. Smith of the Research Laboratory of the Leeds and Northrup Co. several samples of exceedingly pure nickel. I have no analysis of the nickel, but its high purity is vouched for by the unusually high value of the temperature coefficient of electrical resistance, which between 0° and

100° was 0.00634, against 0.0049 for commercial nickel over the same range. Two longitudinal flow samples were made from this pure material.

The first of these samples gave points lying on three different lines separated by the usual 5%. The slope corresponded to a decrease of conductivity of 13.5% for 12000 kg. In setting up the second sample I made the attempt to prevent motion of the thermo-couple wires in the holes with a piece of 0.002 inch wire laid beside them, as has been

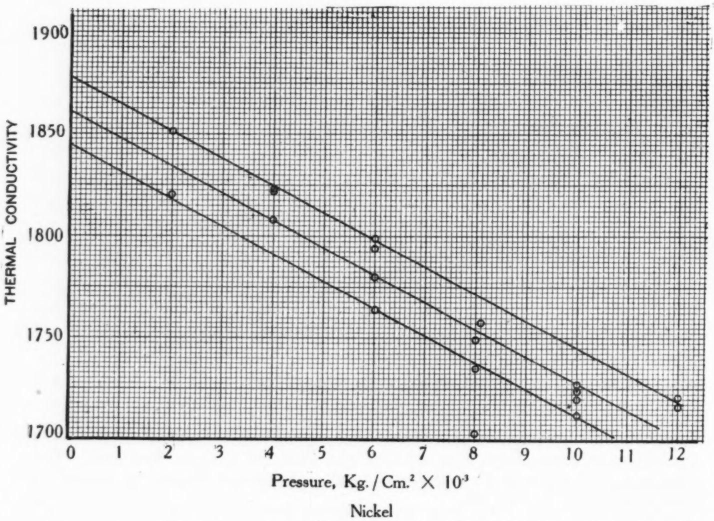

FIGURE 9. Nickel. Thermal conductivity in arbitrary units against pressure in thousands of kg/cm². Results obtained with a longitudinal flow specimen. The points lie on several lines of the same slope; the reason for this is explained in the text.

mentioned in the description of the method. This was the first attempt, and as often happens, succeeded better than subsequent attempts. For some reason I was fortunate enough to get the wire into place without introducing strains into the thermo-couples, and the results showed a gratifying regularity. The results of the final run with this second specimen are shown in Figure 9. It is seen that the readings still lie on three different lines, but these lines are now

separated by much less than 5%, as is to be expected. A partial run with this same specimen, which had to be discontinued because of leak and also because of short circuit in the three-terminal plug, gave exactly the same slope for those readings which could be obtained as the final run. The change shown by this second sample was a decrease of conductivity of 14.5% for 12000 kg., agreeing fairly well with the first sample. Since the second sample gave somewhat more regular results, it is given greater weight in the mean, which I take as 14.1%. The total correction for the effect of pressure on the transmitting medium was 5% of the total conductivity, amounting to about 33% of the observed change under 12000 kg.

The results found above give for the pressure coefficient of thermal conductivity -0.0_412. There are no previous results for comparison.

An incidental result obtained from the measurements with commercial and pure nickel was a comparison of the absolute thermal conductivities. The longitudinal flow method is not well adapted to give the absolute conductivity because of the uncertainty in the corrections for loss through the leads, etc. (the absolute conductivities directly calculated average about 5% higher than the values of Jaeger and Diesselhorst), but the comparative values of absolute conductivity of different materials should be nearly correct. The thermal conductivity of the two samples of pure nickel was found to be 37% higher than that of the two samples of commercial nickel. Considerable confidence may be put in these values, as the individual readings were very consistent; the two samples of pure nickel gave results differing by less than 0.5%, and the results on the two samples of commercial nickel were identical to three significant figures.

Platinum. Measurements were made on two different samples by the longitudinal flow method. The material was obtained from Baker, the purest which they could supply. I have no analysis, but have the statement of Baker that the impurity is guaranteed to be less than 0.1% and is probably not greater than 0.01%.

The measurements on platinum were scattered on three lines of a maximum separation of about 5%, as is usual with this method. The two specimens gave identical results, a decrease of conductivity of 1.9% for a pressure change of 12000 kg/cm^2. The observed effect was positive, but the correction for the effect of the transmitting medium is so large, 5.2%, as to alter the sign of the result.

The pressure coefficient of thermal conductivity as given by the above measurements is -0.0_516. The pressure coefficient of electrical conductivity at 30° between 0° and 12000 kg. is $+0.0_5186$.

Bismuth. An attempt was made to obtain measurements on this metal by the radial flow method, but without success. It did not prove possible to get sufficiently good thermal contact with the fine copper tubing, and I have already mentioned that the attempt to use silver tubing failed because of the extremely rapid alloying action between silver and bismuth. Measurements were finally made on three different specimens by the longitudinal flow method.

A great deal of time was spent in the endeavor to obtain pure material. In my previous work on the effect of pressure on electrical resistance I had purified the metal by electrolysis. I now endeavored to repeat this, but without success; I could not make the bismuth form a coherent deposit. The procedure of the previous work was exactly repeated as far as I could tell. Previously the hydrosilicofluoric acid had been obtained from a German source; this was no longer available and acid from the J. T. Baker Chemical Co. was used instead. The acid was of high purity as indicated by the analysis on the label, but there is a possibility that some impurity not covered by the analysis might have been responsible. I then obtained some bismuth from the U. S. S. Metals Refining Co. I have to thank them for supplying me with six pounds of the metal, in two lots. Their product is prepared electrolytically, in distinction from the ordinary commercial product, and is guaranteed by them to have less than 0.1% impurity. Ordinary commercial bismuth has about 3% impurity. My test for purity has been the temperature coefficient of electrical resistance. This electrolytic bismuth showed a very low coefficient, only 0.0022 between 0° and 30°. Ordinary commercial bismuth is higher. Professor F. A. Saunders was kind enough to make a spectroscopic analysis; he found a very strong silver line, which seemed to indicate a rather considerable impurity. I consulted the U. S. S. Metals Refining Co. again, and they were so kind as to send me a second sample, which they had submitted to chemical analysis, and found to contain only silver in detectible quantity, and this was less than 0.06%. But the temperature coefficient of this new sample was again very low. I attempted a purification by slow crystallization from the melt, with the result of bringing the coefficient up to only 0.0025. Ordinary commercial material, purified in the same manner, showed a coefficient of 0.0034. Professor Saunders was again kind enough to make a spectroscopic analysis and found again the strong silver line, which seemed to him could only arise from a rather large amount of impurity. He found traces of Cu and Pb, and no traces of Sn, Cd, Zn, Li, As, or Sb. Professor G. P. Baxter

was now so kind as to make a quantitative determination of the silver, and found 0.03%, confirming the conservative estimate of the U. S. S. Metals Refining Co. I now succeeded in finding a small residue of my original electrolytic bismuth, and Professor Saunders made a spectroscopic analysis of this. He could find only traces of Cu and Pb, the Cu being stronger than in the commercial electrolytic bismuth, and some silver, evidently considerably less than in the commercial. The conclusion seems forced that a quantity of silver as small as 0.03% can depress the temperature coefficient to half the normal value, thus exerting an effect very much greater than such impurities as Pb and Sn, which are present in ordinary commercial bismuth. That difficulty would be expected in removing the silver by recrystallization is evident on an inspection of the mixed crystals diagram for these two metals. This would also be indicated by the energetic alloying of silver and bismuth, which made impossible the preparation of the radial flow specimens.

Under the circumstances it seemed that the best thing to do was to use the commercial electrolytic bismuth, with its known analysis of 0.03% of silver, in the expectation that the effect of this small impurity is abnormally high on the temperature coefficient of resistance. I had previously found that the effect of impurity on the pressure coefficient of resistance is much less than on the temperature coefficient of resistance.

The samples were made from $\frac{1}{8}$ inch wire which had been formed by hot extrusion in the regular way. One advantage of forming the specimen by extrusion is that the crystalline structure is very much finer than when the specimen is cast, and so the results are much more likely to give the average for all the directions of a single crystal.

The thermo-couple holes were drilled in these specimens in the regular way, but a modification was necessary in mounting the heating element. Previously the heating element was mounted in a copper capsule, which was cemented into a hole drilled in the end of the specimen. This was no longer possible, because the capsule was so large that it was not possible to drill a hole to receive it without breaking out the walls in so brittle a material as bismuth. The heating element was accordingly placed in a smaller hole drilled directly in the end of the specimen. This has the disadvantage that the terminal conditions of temperature are not so accurately defined as with the other metals, and the motion of the heating element in its receptacle may produce other irregularities. This was indeed the fact; the points were more scattered than with the other metals, and

the width of the band of scattering was greater than the 5% usually found. The magnitude of the scattering varied with the specimen, as it might be expected to.

In setting up the first sample, the ground of the heating element was made to the sample itself. It has been previously explained that this introduced an effect due to the Peltier heat, which is unusually large for this metal. The mean of readings with two directions of the heating current should eliminate this effect. With the other two samples an independent ground was used, and the effect disappeared.

It is to be expected that if there is any error due to heat leak along the thermo-couple wires that it will be especially large for this metal, whose own thermal conductivity is so small. In order to test this point, duplicate runs were made on the third sample, first with the ordinary copper-constantan couple, and then with a couple of "therlo" constantan. Very nearly the same results were found, showing the adequacy of the precautions taken to prevent leak along the couple wires.

The third sample gave the most regular results; probably some accidental twist or bend in the wires made them less likely to be displaced under pressure than those of the other samples. The results with this sample are reproduced in Figure 10.

The results found with the different samples are as follows: #1, -38.8% for 12000 kg.; #2, -38.8%; #3 (copper-constantan couple) -37.3%, and #3, (therlo-constantan couple) -35.5%. Mean -37.8%. Because of the low conductivity of bismuth the correction for the transmitting medium is large, amounting to 13.8%, and is in the direction to make the true effect more negative than the observed effect.

The pressure coefficient of thermal conductivity to be deduced from the above measurements is -0.0_431. It is to be noticed that this is negative, and also that it is abnormally high. The abnormal sign agrees with the pressure effect on electrical conductivity, which also decreases under pressure. I found at 30° the average pressure coefficient of electrical resistance up to 12000 kg. to be -0.0_4212. Bismuth was not among the metals measured by Lussana, so there are no previous results for comparison.

Antimony. Measurements were made on four samples, all by the longitudinal flow method. The material was obtained from the J. T. Baker Chemical Co. It was supposed to be especially pure, although I have no analysis. Antimony from the same source was formerly used by the Bureau of Standards to give a fixed melting point, but

their experience was that although the chemical analysis might show very little impurity, there was nevertheless present in all antimony from American sources some slight impurity which was sufficient to displace the melting point by several degrees. Presumably my antimony suffered from the same impurity.

Two of my samples were made from cast antimony and two from extruded metal. The metal was cast by pouring it into a groove in a massive iron block to a thickness of a trifle over $\frac{1}{8}$ inch. The chilling was hence very rapid, and the crystalline structure very fine. From

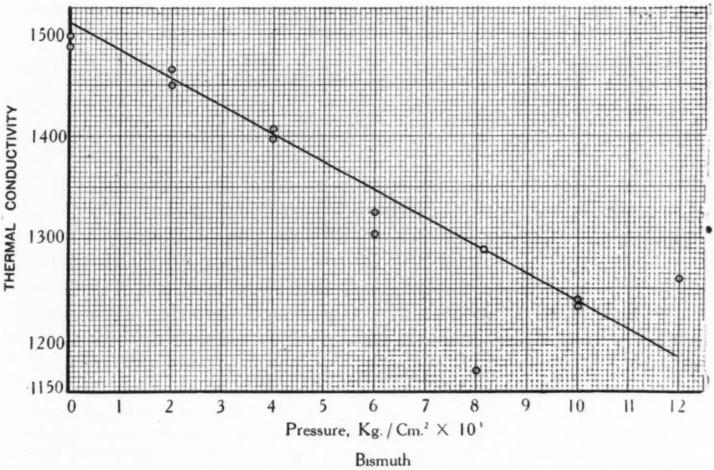

FIGURE 10. Bismuth. Thermal conductivity in arbitrary units against pressure in thousands of kg/cm^2. Results obtained with a longitudinal flow specimen.

this casting two pieces were machined for the longitudinal flow method. The metal is so brittle that it was not possible to cut it with the tool in the ordinary way, but the machining had to be by grinding. Even then extreme caution was necessary, and there were many failures before success was attained. The wire for the other two specimens was extruded at a red heat through a high speed steel die of the required dimensions. Some little practice was needed before the proper manipulation was found. It is possible to extrude antimony at a considerably lower than a red heat, but with a wire as large as $\frac{1}{8}$

inch the product is likely to be very brittle, or break spontaneously into small pieces. If the temperature is raised very close to the melting point, however, it is possible to get by extrusion a uniform straight wire with no apparent flaws, and not as brittle as the casting.

The thermo-couple holes were drilled in the four pieces in the regular way. The heating elements, as in the case of bismuth, were mounted directly in small holes drilled in the ends, it not being feasible to drill so large a hole as the use of the copper capsule would have demanded. This manner of attaching the heating element was responsible for the greater irregularity of the points, as also in the case of bismuth. In one case the scattering was such and the accidental

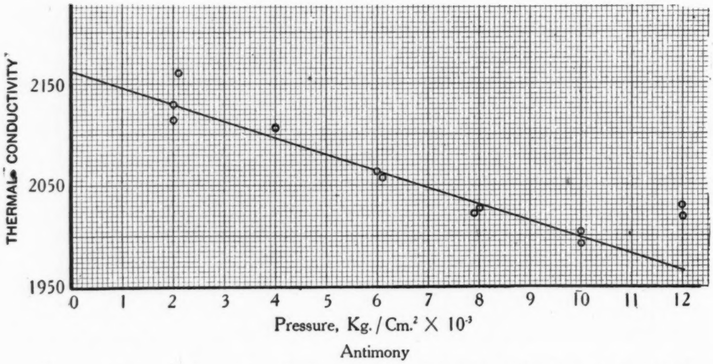

FIGURE 11. Antimony. Thermal conductivity in arbitrary units against pressure in thousands of kg/cm². Results obtained with a longitudinal flow specimen.

distribution such that a positive sign for the effect might have been suspected.

The readings obtained with the first of the cast specimens were the most regular; these are reproduced in Figure 11. The thermo-couple used with the second of the extruded specimens was therlo-constantan, instead of copper-constantan. The readings with this were essentially the same as with the others, thus again showing freedom from heat leak along the wires of the couple.

The thermal conductivity decreases with rising pressure; the two cast specimens gave respectively −23.9 and −26.3%, and the two extruded specimens −24.8 and −23.9%. The mean of all four is

-24.7%. It is to be noticed that within the limits of error no difference is to be detected between the cast and the extruded specimens.

The pressure correction for the transmitting medium was 15.3% on the total conductivity; this means that the final corrected result was three times as large as the observed pressure effect.

The above results give for the pressure coefficient of thermal conductivity -0.0_421, larger than for any other metal except bismuth. I have previously found that the electrical conductivity of antimony also decreases with rising pressure, and at 30° the average coefficient to 12000 kg. is -0.0_4108.

Lussana has also measured the effect of pressure on the electrical and thermal conductivity of antimony, and his results are in precise disagreement with mine. He finds that the electrical conductivity increases under pressure, as it does for normal metals. At 25° his coefficient, presumably to 3000 atmospheres, is 0.0_5874. There must be something vitally wrong here; measurement of electrical resistance under pressure should offer none of the difficulties of thermal conductivity, and there should be no reason for a disagreement as to sign between different observers. The relation between pressure and thermal conductivity Lussana finds to be distinctly not linear. The initial change is at a rate corresponding to a coefficient of 0.0_5251, and at 3000 the rate corresponds to a coefficient of only 0.0_5164. So large a departure from linearity in a metal with as high a melting point as antimony is without precedent. It does not seem improbable that the sign that Lussana found for the coefficients of both electrical and thermal conductivities may be due to a closing of minute fissures between the crystalline grains under pressure, such as Borelius and Lindh found for bismuth.[5] The departure of his thermal conductivity from linearity is in accord with this suggestion.

Petroleum Ether. It has already been explained that it was necessary to determine the absolute conductivity and pressure coefficient of this substance in order to obtain the correction due to the effect of pressure on the transmitting medium in the longitudinal flow method. The method adopted for determining these constants for petroleum ether was a radial flow method, and demanded very little change in the apparatus already used for metals. The apparatus is shown in Figure 12. It consists of an inner cylinder of copper held concentrically within an outer hollow cylinder, which in turn fits closely inside the pressure cylinder, and is maintained concentric with it by the same spring device that was used for the metals. The petroleum ether fills the annular space between the two copper cylinders. The

axis of the central cylinder contains a linear source of heat, that is a wire carrying a current, precisely as for the metals. The difference of temperature between the outer surface of the inner cylinder and the inner surface of the outer cylinder is measured by thermo-couples. These were of the same construction as for the metals, and were mounted in fine copper tubes, which were sweated into small holes drilled lengthwise of the cylinders. Of course with this construction the couples could not be located exactly on the surface of either cylinder, but the thermal conductivity of the copper is so much higher than that of the petroleum ether that practically all the temperature drop takes place across the annular space of the liquid, and a rough computation shows that with the dimensions used any error from this cause is negligible. As a precaution against failure of perfect geometri-

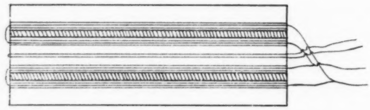

FIGURE 12. Longitudinal section of the apparatus for measuring the thermal conductivity of petroleum ether. The liquid is shown shaded between copper cylinders, with a central heating unit and two sets of thermal junctions bridging the liquid.

cal centering of the inner cylinder in the outer one, three couples instead of one were used, spaced at even angular intervals around the cylinders, and these were connected in parallel, so that the reading obtained gave the mean of the temperature differences around the cylinder, and any geometrical imperfection is eliminated. The annular space between the cylinders was only 1.3 mm. wide. This is so narrow as to remove any error from convection in the liquid, even at atmospheric pressure, and it has already been explained that such error vanishes at higher pressures because of the rapidly increasing viscosity. No effects were found in the measurements to suggest error from such a source.

Because of the substantial equality of temperature throughout the copper cylinders, it is to be expected that errors from slight changes in position of the thermo-couples, which played so large a part in the measurements of the metals, would vanish. This is indeed the fact, and the measurements showed a high degree of regularity, much beyond that obtained for any metal.

In making the readings, the entire interior of the apparatus was

filled with petroleum ether. The same method would serve for any other liquid which does not absorb impurity, or become conducting under pressure. Unfortunately most of the liquids whose other properties are best known, and which it would be most interesting to measure, such as the alcohols, are not of this kind. To determine the thermal conductivity of these under pressure it will be necessary to so modify the apparatus that the liquid can be insolated from the electrical leads.

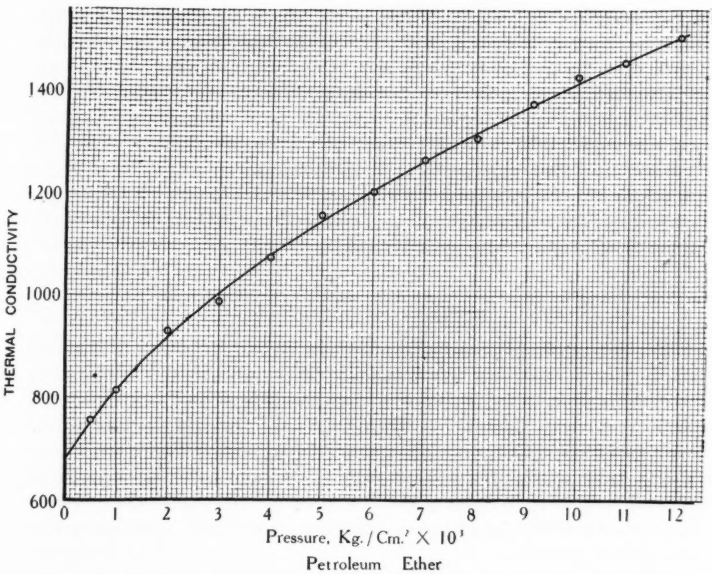

FIGURE 13. Petroleum Ether. Thermal conductivity in arbitrary units against pressure in thousands of kg/cm². Results were obtained with the apparatus of Figure 12.

The observed results with petroleum ether are shown in Figure 13. The greater regularity of the results as compared with the metals is manifest. The lowest pressure of these readings was 500 kg. The reason for not going to atmospheric pressure was not error from convection currents, but because at this pressure the heating effect would have been sufficient to vaporize the ether, and so introduce error.

The effect of pressure is seen to be a large increase of conductivity, amounting at 12000 kg. to an increase of 2.22 fold. The increase is not linear with pressure, but there is a departure from linearity in the normal direction, in that the change becomes proportionally less at the higher pressures.

The initial rate corresponds to an increase of conductivity of about 20% per thousand kg. So far as order of magnitude goes, this agrees with Lussana, who found the correction for his transmitting medium to be at the rate of 30% per thousand kg. He did not find a departure from linearity. Of course there is no reason to expect more than agreement as to order of magnitude, because his transmitting medium was a comparatively heavy oil, quite different in properties from mine.

The measurements of the effect of pressure on the thermal conductivity of liquid is a thing worth doing for its own sake, and I hope to get the chance to make measurements on a number of others. In fact I already have results for two alcohols and kerosene. Suffice it here to mention that there seems to be an intimate connection between the pressure effect on thermal conductivity and the pressure effect on the velocity of propagation of sound.

General Comment on Lussana's Results.

The only previous measurements of the effect of pressure on thermal conductivity are those of Lussana. Since his results often differ essentially from mine, even as to sign, and since this is a matter of considerable importance for theoretical considerations, some critical survey of his results seems called for. In general, Lussana finds that the thermal conductivity of all metals increases under pressure, and this increase is nearly the same as that of the electrical conductivity, so that the Wiedemann-Franz ratio remains nearly constant under changes of pressure.

Lussana's method was an adaptation to high pressures of one originally due to Depretz and Biot. A long bar of metal has a source of heat at one end and is immersed in a medium through which the heat may flow away laterally. The temperature of the bar, which is assumed constant across the section, is measured at three equi-distant points along it, and in terms of the two differences of temperature thus obtained, a relation can be found between a certain geometrical factor and the ratio between the thermal conductivity and the lateral conductivity into the surrounding medium. The essential difference between this method and mine is that in mine there is a source at one end of the bar and a sink at the other, so that nearly all the heat input

flows through the bar and out at the other end, and only a comparatively small part is lost laterally to the surroundings; whereas with Lussana all the heat input flows out laterally. In Lussana's method the correction for the effect of pressure on the transmitting medium affects directly the entire heat input, whereas in my method the pressure correction is to be applied only to that part of the heat input which escapes laterally.

My most serious criticism of Lussana's method concerns this correction for the transmitting medium. The magnitude of the correction is about 30% per thousand kg., whereas the order of magnitude of the changes of thermal conductivity of the metals is at most only 3%, or one tenth of this. This demands that the effect of pressure on the transmitting medium be known ten times well as the final result for the metal. Nevertheless, Lussana determined the correction for the liquid to only one significant figure; as a matter of fact there is a misprint in his paper, which made the correction appear to be at the rate of 300% for one thousand kg. I inquired about this in a letter to Lussana, and he told me that the decimal point had been displaced one figure, and that the correct result was 30%, agreeing with my own results as far as order of magnitude goes. Having determined the correction to one significant figure, not even noticing the departure of the effect from linearity with pressure, Lussana gives his coefficient for metals to three significant figures. Three significant figures for the metal would have demanded at least four significant figures in the correction.

Lussana states that his results were computed from the observations by the method of least squares; he does not anywhere reproduce a single set of observations, nor does he state the probable error of his results, surely a significant omission considering the method of computation. There is no clue in his paper to the accuracy to be attached to his results.

There seems to be almost no correlation between Lussana's results and my own. In only one case, that of zinc, do we find the same sign for the change produced by pressure in the Wiedemann-Franz ratio. It seems to me that for the present we are justified in assuming that there are large errors in Lussana's results.

Discussion.

Probably the most significant theoretical conclusions from the above data may be derived from the pressure coefficient of the Wiedemann-Franz ratio. The classical electron theory would lead us to expect that the coefficient would be zero, since the ratio is the same for

all metals at the same temperature, and the same metal under different pressures at the same temperature is merely a special case of two different metals. As a matter of fact the ratio is not constant, but may either increase or decrease with increasing pressure; in the majority of cases it decreases. The average values of the coefficient between 0 and 12000 kg. are shown in Table III.

TABLE III.

Metal	Pressure Coefficient of Wiedemann-Franz Ratio
Pb	$+0.0_{5}6$
Sn	$+0.0_{5}3$
Cd	$-0.0_{5}17$
Zn	$-0.0_{5}25$
Fe	$-0.0_{5}26$
Pt	$-0.0_{5}35$
Ag	$-0.0_{5}70$
Cu	$-0.0_{5}93$
Ni	$-0.0_{4}13$
Sb	$-0.0_{4}10$
Bi	$-0.0_{4}10$

My own theory of electrical conduction attempted to explain the Wiedemann-Franz ratio,[6] and to do this, I imagined the same sort of mechanism of conduction as the classical theory. I still can see no reason to suppose that the most important part of heat conduction is not as imagined by the classical theory; the success of the theory in accounting for the numerical value of the ratio, which is approximately constant for the different metals, (it may vary from 6.38×10^{10} for aluminum to 9.14×10^{10} for bismuth), is too striking to be put aside with no substitute. At the same time it is evident that the account given by the classical theory cannot be complete; no account has been taken of the conduction by the atoms, and the agreement of the theoretical with the experimental value is not as close as we must demand of a finished theory.

It is natural to look to the still unexplained part of thermal conductivity to account for the departures from constancy of the Wiedemann Franz ratio under pressure. The part of the conductivity

which is due to the electrons would be expected to have the same pressure coefficient as the electrical resistance (except for a possibility to be mentioned later); the remaining part must be capable of either positive or negative variation under pressure, and must be of the right order of magnitude.

In the first place, let us consider the possible magnitude of the non-electronic part of heat conduction. The first deduction of the theoretical value of the Wiedemann-Franz ratio, given by Drude, was an elementary one, in which certain simplifying assumptions were made, particularly that the velocities of all the electrons were the same. Later Lorentz gave a more exact discussion, taking account of the Maxwell distribution of velocities among the electrons, and obtained a value for the ratio only two thirds of that of Drude. The discussion of Lorentz has later been verified by Bohr and others. The elementary value for the ratio is much closer to the experimental values than the more rigorous one, but still lies somewhat low. The failure of the more exact value to agree more closely with the facts has been regarded by some as a blot on the classical theory, but by others is regarded rather as to the credit of the theory, because the Wiedemann-Franz ratio as calculated by the elementary theory was felt to be too close to the experimental value to sufficiently allow for the atomic part of the conduction.

I shall take this latter point of view, and consider that the value for the Wiedemann-Franz ratio calculated by Lorentz represents the part due to electronic conduction, and that the difference between this theoretical value and the actual value represents the part of the heat conduction that must be accounted for in other ways. This point of view at once imposes certain numerical limits on the changes under pressure that it should be possible to obtain experimentally. For the total change of thermal conductivity under any pressure must never be so great as to more than wipe out the part of the conductivity which was initially ascribed to the non-electronic part. This means that the total decrease of thermal conductivity, after allowing for a change equal to the change of electrical conductivity, must not be greater than the difference between the total initial thermal conductivity, and the part given by Lorentz's expression. In practise this imposes a restriction only when the thermal conductivity increases under pressure less rapidly than the electrical conductivity. An examination of the results obtained in this paper will show that this condition is met in all cases. The condition imposed is most restrictive in the case of nickel. Under 12000 kg. its thermal conductivity decreases by 14.5%,

and the electrical conductivity increases by 1.8%. The sum of these, 16.3%, is an upper limit which the fractional part of the total conductivity due to the non-electronic part must not exceed. Now the theoretical value for the Wiedemann-Franz ratio is 4.3×10^{10} (Lorentz's value), and the experimental value for nickel is 6.99×10^{10}. This allows the possibility of 39% of the thermal conductivity initially being of non-electronic origin, which is more than twice the extreme set experimentally. It would seem that under these conditions, when so comparatively large a part of the atomic conductivity has been wiped out by pressure, that the relation between conductivity and pressure must depart from linearity. The experimental accuracy was not great enough, however, to show such a departure.

Further consideration of the theoretical significance of these results is reserved for a forthcoming paper in the Physical Review.

Summary.

Two methods are described for measuring the thermal conductivity of metals under pressure. The first of these is a radial flow method, which has many theoretical points of advantage, but is of limited applicability in practise because of the difficulty of getting metals in a condition of sufficient homogeneity. The second is a longitudinal flow method, the essential of which is the small size of the specimen. The irregularities of the individual readings by the second method are greater than by the first method, but the effect of inhomogeneities is less and different specimens of the same metal will give the same result.

Measurements of the effect of pressures to 12000 kg/cm^2 on the thermal conductivity of 11 metals have been made by one or the other of these methods. The effect may be either positive or negative, and is more often negative than positive. In only two cases, lead and tin, does the Wiedemann-Franz ratio increase under pressure; for the other metals it decreases, and sometimes by large amounts. In addition to the metals, the pressure coefficient of thermal conductivity of petroleum ether has been measured. The conductivity increases by a factor of about 2.2.

The only previous measurements have been by Lussana, who obtained results entirely different from those found here. His method is criticised in some detail, chiefly on the basis of the uncertain correction for the lateral loss of heat to the pressure transmitting medium.

These results indicate that a fairly large part of thermal conduction

in a metal is performed by the atoms. Theoretical reasons are given for estimating the atomic contribution to the thermal conductivity as 50 per cent of the electronic contribution.

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The Jefferson Physical Laboratory,
Harvard University, Cambridge, Mass.